

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Halofluorination of Hydrocarbons

5 W. G. LAPORTE CHEMICALS LIMITED, a British Company, of Kingsway, Luton, Bedfordshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for preparation of halogenated hydrocarbons, and more particularly for the preparation of halo-fluoro derivatives of hydrocarbons containing from one to fifteen carbon atoms.

15 The present invention provides a process for the halofluorination of hydrocarbons selected from straight chain saturated hydrocarbons and straight chain ethylenically unsaturated hydrocarbons each having up to 15 carbon atoms in the molecule, which comprises the step of reacting the hydrocarbon in the vapour phase and at a temperature of from 200 to 650° C. simultaneously with hydrogen fluoride and chlorine, bromine or iodine in a reactor in the presence of elemental carbon and, at least when the process is the chlorofluorination of 20 methane, in the absence of any metallic halide catalyst; the reaction being conducted at a pressure of at least 0.5 atmosphere and with a residence time of reactants in the reactor being from 0.1 to 200 seconds.

25 30 The term halofluorination employed herein refers to chlorofluorination, bromofluorination or iodo-fluorination and the term halofluoro-hydrocarbons similarly refers to chlorofluoro-hydrocarbons, bromofluoro-hydrocarbons or iodo-fluoro-hydrocarbons.

35 The carbon employed can be activated or non-activated and can be of any particle size or porosity which does not cause blockage in the reactor. It can be employed as a static bed or 40 as a fluidised bed.

The conditions of reaction temperature

[Price]

and pressure and residence times are of course interrelated but the general requirements are that the temperature shall be from 200 to 650° C., preferably from 400 to 550° C. The halogenation proceeds most effectively above 400° C., incomplete replacement of hydrogen by halogen being likely below 400° C. As the temperature is raised, degradation of the reaction product tends to occur, the degradation being substantial at temperatures over 550° C. and undesirably great above 650° C. The desired temperature can be achieved for example by external heating of the reactor and/or by preheating at least one of the gases or vapours to be introduced.

45 50 55 As previously stated, as the reaction temperature is raised degradation of the reaction product tends to occur. This feature of the process can be turned to advantage in that by suitable choice of reaction temperature, residence time and proportions of the reactants it is possible, when the hydrocarbon used contains from 3 to 15 carbon atoms, to produce a product consisting of or containing at least one chlorofluoromethane. This embodiment of the process is illustrated in Example 15 herein.

60 65 70 Since the reactant halogen and hydrocarbon may react violently at elevated temperature, it may be preferred either to maintain the part of the carbon bed at which they are introduced below the optimum temperature required for the reaction and/or to introduce a diluent gas. The diluent gas can be, for example one or more of an inert gas such as nitrogen, hydrogen halide produced in the reaction or other recycled gaseous products of the reaction, or hydrogen fluoride in excess of that required for the reaction.

75 80 85 The residence time in the reactor is defined

1,077,932

2

as the ratio of the total volume in ccs. occupied in the reactor by the carbon bed (including free volume in the carbon bed), to the total rate of introduction of gas into the reactor, 5 in ccs. per second; the volume of gas introduced into the reactor being measured at the reaction temperature and pressure.

It is usually most convenient to carry out the process at approximately atmospheric pressure, unless the product separation is to be carried out at elevated pressure when it may be found more convenient to operate the halogenation at the same pressure as the separation. Elevated pressure within the range 5 to 15 atmospheres will usually be convenient for the separation.

We have found that when operating within the preferred ranges of conditions the halogenated reaction product is usually a mixture of various per-halogenated compounds and a particular advantage of the process is that it provides high yields of the perhalogenated compounds. The prefix "per" is employed here to indicate the absence of hydrogen in the compounds.

It is possible by varying the temperature, residence time and proportion of reactants, to alter the proportion of the particular compounds obtained, and it is also possible under less drastic conditions to obtain halofluoro-compounds containing hydrogen. Similarly under more drastic fluorination conditions it is possible to obtain perfluoro-compounds. In general it is possible to increase the ratio of compounds with high fluorine content (for example CClF_3) to compounds with low fluorine content (for example CCl_3F) by employing an increased temperature, of from 400 to 550° C., an increased residence time 40 within the stated range of from 0.1 to 200 seconds, or an increased ratio of hydrogen fluoride to hydrocarbon.

The halogenated compounds can be separated from the product gas stream, which 45 may contain diluent gas or unconverted reactants, by fractional distillation or other known methods.

In one aspect, the present invention provides a process for the halogenation of methane 50 wherein the methane is reacted simultaneously with hydrogen fluoride and chlorine, in a suitable reactor at elevated temperature in the presence of elemental carbon and in the absence of any metallic halide catalyst; the 55 reaction being conducted in the vapour phase, and the temperature pressure and residence time being such that there is in the product at least one chlorofluoromethane.

In this aspect of the invention, the temperature within the reactor is within the range 60 200 to 500° C., preferably 400 to 500° C., the residence time is preferably within the range 10 to 100 seconds, and the pressure within the range 0.5 to 2 atmospheres, unless

the products are to be separated under elevated pressure.

The process of the present invention is particularly suited to simultaneous treatment of methane with hydrogen fluoride and chlorine. Surprisingly the main products of this reaction are the extremely useful compounds trichloromonofluoromethane and dichlorodifluoromethane.

In the further aspect of the invention which relates to the chlorofluorination of straight chain saturated or ethylenically unsaturated hydrocarbons having from 2 to 15 carbon atoms in the molecule, the temperature is preferably from 200 to 600° C., the residence time is preferably from 1 to 100 seconds and the pressure about atmospheric pressure, unless the products are to be separated under elevated pressure.

Surprisingly the product obtained from hydrocarbons having from 2 to 15 carbon atoms in the molecule usually contains both saturated and unsaturated materials whether or not the starting material was saturated.

The reactor should, of course, be constructed from materials which are resistant to attack by the reaction mixture. Suitable materials are stainless steel, nickel, Monel, Inconel, Hastelloy, (the terms Monel, Inconel and Hastelloy are registered Trade Marks) or metal lined with carbon. The reactor can be for example in the form of a tube, the reactants being introduced at or near one end and the products passing out at or near the other end. Oxygen can if desired be removed before the reaction by flushing the reactor with the diluent gas referred to above.

A form of apparatus suitable for the reaction comprises a substantially vertical cylindrical stainless steel column containing a static carbon bed. The column is enclosed in a jacket which contains heating coils. An entry tube for the reactants is situated at the top of the column. An outlet leads from the base of the column through a polyethylene vessel, thence through a KOH scrubbing tower, a water condenser, a silica gel drying column and two traps cooled in a solid carbon dioxide/acetone mixture.

In operation, the reactants are mixed and fed into the top of the heated reactor. The polyethylene vessel acts as a trap for any compounds of high boiling point in the product, (the "high boiling" fraction); the hydrogen halide produced by the reaction and any unreacted hydrogen fluoride in the product are removed in the KOH scrubber, the water condenser removing any water carried over from the KOH scrubber, and the remainder of the product (the "low boiling" fraction) is condensed in the solid carbon dioxide/acetone trap.

In one preferred embodiment of the invention there is maintained in the reactor a tem-

perature gradient rising from below the reaction temperature to the reaction temperature and in which at least one of the reactants is introduced into the reactor at a temperature below the reaction temperature. In another embodiment all the reactants are introduced into the reactor in admixture and at a temperature below the reaction temperature.

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In certain cases an advantage may be gained in the reaction with hydrocarbons having from 2 to 15 carbon atoms in the molecule by the presence of a metallic halide catalyst which may be carried on the carbon.

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The mixture of products obtained using ethane is substantially the same as that given by ethylene. With both starting materials the product usually includes the following compounds:

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1,2,2-trifluoro-1,1,2-trichloro-ethane;
1,2-difluoro-1,1,2,2-tetrachloro-ethane;
1-fluoro-1,1,2,2,2-pentachloro-ethane per-
chloroethylene and trichloroethylene.

We have found that under similar conditions products obtained from propane and propylene contain a greater proportion of fluorinated products than do the products obtained from ethane and ethylene. The products given by propane and propylene are for example 1,1,1-trifluoro-2,3,3-trichloro-prop-2-ene; 1,1,1-trifluoro-3,3-dichloro-prop-2-ene and 1,1,1-difluoro-1,3,3-trichloro-prop-2-ene, and in addition, if fragmentation has taken place,

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perchloroethylene, monofluorotrichloro-methane and di-fluoro-dichloro-methane are also obtained. 1,1,1-Trifluoro-2,3,3-trichloro-prop-2-ene and 1,1,1-trifluoro-3,3-dichloro-prop-2-ene can both be oxidised to the extremely useful compound trifluoroacetic acid.

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It has also been found that when pentane is reacted simultaneously with hydrogen fluoride and chlorine in accordance with the process of the invention the reaction product may contain over 90% by weight of cyclic chlorofluoro compounds.

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Accordingly the present invention also provides a process for the production of cyclic chlorofluoro-compounds having a five-membered carbon ring wherein n-pentane is reacted in the vapour phase at a temperature of from 200 to 650° C. simultaneously with hydrogen fluoride and chlorine in a reactor in the presence of elemental carbon, the reaction being conducted at a pressure of at least 0.5 atmospheres and with a residence time in the reactor of from 0.1 to 200 seconds.

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The reaction product from a hydrocarbon selected from hydrocarbons containing from 4 to 15 carbon atoms in the molecule is a complex mixture of halogenated compounds.

Isolation of these compounds from one another is a lengthy process but we have been able to establish that in all cases the product is highly fluorinated and almost always contains some unsaturated compounds.

The extent of the fluorination in the product from hydrofluoric acid, chlorine and various hydrocarbons is shown in table 1.

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TABLE 1

Amount of fluorine % weight/weight

Starting material	"High boiling" fraction	"Low boiling" fraction
n-butane	13.1	36.4
butadiene	13.1	35.4
n-pentane	15.6	25.2
n-heptane	19.2	38.0
n-nonane	19.7	—
C ₁₄ —C ₁₅ paraffin mixture	18.3	—

In the case of n-nonane and the C₁₄/C₁₅ paraffin mixture no product was obtained in the solid carbon dioxide/acetone trap. However analysis of the gas stream leaving the trap showed that chlorofluorocompounds of low molecular weight (for example trichlorofluoromethane and dichlorodifluoromethane)

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were present, indicating that cleavage of the starting material has occurred.

Starting material with the same number of carbon atoms, whether saturated or not, give substantially the same products. For example, as shown in the table, in a typical run starting with butane, the amount of fluorine in the

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- high boiling product was 13.1%, by weight and in the low boiling product 36.4%, by weight, whilst starting with butadiene the figures were 13.1% and 35.4% respectively. The products from both butane and butadiene contained the same degree of saturation, and analysis by vapour phase chromatography and infra-red spectroscopy showed that the product from butane was markedly similar to that from butadiene.
- The following Examples illustrate some applications of the invention, when carried out on a laboratory and pilot plant scale.
- EXAMPLE 1.**
- The reactor employed for this Example and for Examples 2 to 11 was a vertical stainless steel tube enclosed in an electrically heated jacket. 440 ccs. of granulated coke were packed into the reactor to form a static bed of carbon.
- The reactor was then heated to 440° C. and nitrogen gas was flushed through the reactor at a rate of 54 ccs/min for 2 hours. Methane and chlorine were then introduced into the reactor together with the nitrogen, the methane at a rate of 60 ccs/min and the chlorine at a rate of 240 ccs/min. After passage of methane and chlorine had begun, anhydrous hydrogen fluoride was introduced into the reactor at a rate of 160 ccs/min. Nitrogen was introduced throughout the reaction. The mean temperature in the reactor was 432° C. and the residence time of the reactants was 21.0 seconds. The product leaving the reactor contained hydrogen chloride and a mixture of chlorofluorocompounds.
- The effluent gas stream from the reactor was washed with aqueous caustic potash solution so as to remove the acidic constituents hydrogen chloride, hydrogen fluoride and chlorine. Thereafter the gas stream was dried by bubbling it through concentrated sulphuric acid and the lower boiling point components were condensed from the gas stream by means of an acetone/solid carbon dioxide trap and a liquid nitrogen trap arranged in series.
- The run was continued for four hours, when the acetone/solid carbon dioxide trap contained 31.0 ccs. liquid chlorofluorocarbons and the liquid nitrogen trap contained solids equivalent to 4.2 ccs. liquid chlorofluorocarbons. The main products were trichloromonofluoromethane (CCl_2F) and dichlorodifluoromethane (CCl_2F_2). The ratio of $\text{CCl}_2\text{F}:\text{CCl}_2\text{F}_2$ in the combined product was 2.6:1. The percentage conversion to the desired chlorofluoro-compounds was 74.0% of the methane and 82.0% of the chlorine introduced into the reactor.
- Examples 2—5 below follow the basic pro-
- cedure of Example 1 but have certain differences which are described below.
- EXAMPLE 2.**
- The differences between this Example and Example 1 were that the mean temperature in the reactor was 429° C. and the residence time 21.3 seconds. The product in this Example was again a mixture of chlorofluorocompounds, and the main products were again trichloromonofluoromethane and dichlorodifluoromethane but their ratio in the product was 2.4:1.
- EXAMPLE 3.**
- In this Example the nitrogen was introduced into the reactor at a rate of 104 ccs/min. the mean temperature in the reactor was 428° C., and the residence time was 19.4 seconds. The run was continued for 4.15 hours when the first trap contained 33.2 ccs. and the second trap 9.0 ccs. of product. The ratio of $\text{CCl}_2\text{F}:\text{CCl}_2\text{F}_2$ in the product was 2.0:1 and the percentage conversions of methane and chlorine were 76.5 and 81.0 respectively.
- EXAMPLE 4.**
- In this Example the nitrogen was introduced at a rate of 150 ccs/min and the hydrogen fluoride at 90 ccs/min. The mean temperature was 425° C. and the residence time was 20.4 seconds. The run was continued for 2½ hours when the first trap contained 20.0 ccs. and the second trap 2.7 ccs. of product. The ratio of $\text{CCl}_2\text{F}:\text{CCl}_2\text{F}_2$ in the product was 3.1:1 and the percentage conversion of methane and chlorine were 70.0 and 83.4 respectively.
- EXAMPLE 5.**
- In this Example the nitrogen was introduced at a rate of 200 ccs/min and the hydrogen fluoride at a rate of 130 ccs/min. The mean temperature was 423° C. and the residence time was 17.5 seconds. The run was continued for 13.6 hours when the first trap contained 23.6 and the second trap 6.2 ccs. of product. The ratio of $\text{CCl}_2\text{F}:\text{CCl}_2\text{F}_2$ in the product was 1.6:1. Significant quantities of chlorofluorocompounds containing hydrogen, especially CHClF_2 and CHCl_2F were also produced in this Example. The percentage conversions of methane and chlorine were 71.0 and 82.0 respectively.
- Table 2 summarises Examples 6 to 10 and shows the effect on the product of the chlorofluorination of methane of adjusting the temperature, residence time and proportion of reagents.

1,077,932

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TABLE 2

Reactants (cc./min.)			Diluent (cc./min)	Temperature °C.	Residence time (seconds)	Product (molar %)					
CH ₄	Cl ₂	HF				CCl ₄ F	CCl ₃ F ₂	CCl ₂ F ₃	CHCl ₂ F	CHClF ₂	Others
50	200	200	161	350	18.5	4	11	—	14	28	43
50	200	200	161	405	17.1	21	52	10	4	13	—
62.5	250	250	468	422	10.0	24	37	11	10	18	—
62.5	250	250	3560	422	2.5	28	15	—	27	13	17
125	500	250	155	425	10.0	36	50	4	5	5	—

The diluent in these Examples was nitrogen.

EXAMPLE 11.

In this Example, bromine was substituted for chlorine. The bromine was introduced into the reactor by bubbling nitrogen through liquid bromine. The rates of introduction of the reactants and the diluent were:

methane	20.4 cc./min.
bromine	3.4 cc./min.
hydrogen fluoride	4.5 cc./min.
nitrogen	132 cc./min.

The temperature in the reactor was 420° C., and the residence time was 52 seconds. The product contained a trace of unreacted methane but the remainder was entirely trifluorobromomethane.

EXAMPLE 12.

In this Example the reactor employed in Examples 1 to 11 was replaced by a larger vertical stainless steel tube enclosed in an electrically heated jacket and containing 17

litres of granulated coke. The reactants and diluent gas were introduced at the top of the reactor at the following rates:

EXAMPLE 13.

Example 12 was repeated with the difference that the rate of introduction of diluent was increased to 11,000 cc./min, which reduced the residence time of the reactants to 25 seconds. The run was carried out for 7 hours. The percentage conversion of methane was 87% and the product contained 76.3% trichloromonofluoromethane, 22.4% dichlorodifluoromethane and traces of monochlorotrifluoromethane and tetrafluoromethane.

EXAMPLE 14.

The reactor used in Examples 12 and 13 was again employed but was heated so that the temperature at the top of the bed was about room temperature rising to 350° C half way down the bed and being between

45 methane 1000 cc./min
chlorine 4000 cc./min
hydrogen fluoride 2000 cc./min
diluent 5000 cc./min

50 The diluent which was recycled was initially nitrogen but contained an increasing amount of halogenated methanes as the reaction progressed. The temperature at the top of the reactor was 480° C, falling to 350° C. at the base, and the residence time was 37.5

55 seconds. The products passed out of the base of the reactor, through an aqueous caustic soda solution, were dried by passage over silica gel, and then compressed. The run was continued for 6 hours.

60 The percentage conversion of methane was 62%. The product contained 75% trichloro-

EXAMPLE 15.

In this Example the reactor employed in Examples 1 to 11 was replaced by a larger vertical stainless steel tube enclosed in an electrically heated jacket and containing 17

6

1,077,932

350-400° C. in the bottom half of the bed. The reactants were introduced into the reactor at the following rates:

5	methane	1000 cc./min
	chlorine	4000 cc./min
	hydrogen fluoride	2000 cc./min
	diluent	11000 ccs./min

percentage conversion of methane was 86% and the product contained

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37.5%	trichloromonofluoromethane
59.0%	dichloro-difluoromethane
3.3%	monochlorotrifluoromethane + tetrafluoromethane
0.2%	carbon tetrachloride

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Part of the reaction product was recycled so that the diluent had the following composition (molar %):

15	CCl ₄	0.3%
	CCl ₂ F	11.8%
	CCl ₃ F ₂	45.0%
	CClF ₃	4.0%
	CF ₃	4.0%
	Nitrogen	34.9%

The residence time was 29.4 seconds and the run was continued for 6 hours. The per-

EXAMPLE 15.

The reactor employed was a stainless steel reactor of the type described above having a carbon bed volume of 1000 ccs. and heated to 450° C. The gases in the gas mixture fed into the reactor were introduced at the following rates (measured at room temperature and pressure): nitrogen 48 ccs./min, propylene 87 cc/min, chlorine 522 cc/min and hydrogen fluoride 261 cc/min. The residence time was 25 seconds. The run was continued for five hours. The combined product from the polyethylene and cold traps was a halogenated mixture having the following composition by weight:

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1,1,1-trifluoro-2,3,3-trichloro-prop-2-ene	45.5%
1,1,1-trifluoro-3,3-dichloro-prop-2-ene	34.2%
1,1,3-trifluoro-1,3-dichloro-prop-2-ene	1.5%
perchlorethylene	4.9%
difluorodichloromethane	0.1%
monofluorotrichloromethane	1.2%
others	12.6%

EXAMPLE 16.

A reaction similar to that in Example 15 was carried out using the same apparatus as Example 15 but employing ethane in place of propylene, the temperature of the carbon bed being again 450° C. and the rates of introduction of the gases being as follows (measured

at room temperature and pressure); nitrogen 450 cc/min, ethane 90 cc/min, chlorine 450 cc/min, and hydrogen fluoride 360 cc/min. The residence time was 20 seconds and the run was continued for 7 hours. The combined product from the polyethylene and cold traps had the following composition by weight:—

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1,1-fluoro-1,1,2,2,2-pentachloroethane	14.3%
1,2-difluoro-1,1,2,2,-tetrachloroethane	7.0%
1,2,2-trifluoro 1,1,2-trichloroethane	1.3%
perchlorethylene	61.4%
trichlorethylene	5.2%
others	10.8%

EXAMPLE 17.

Chlorofluorination of pentane was carried out in the reactor described in Examples 15 and 16 being maintained at 450° C. by external heating. The gas stream fed into the reactor was made up of nitrogen (250 cc/min.), pentane (40 cc/min), the flow rates being

1,1,4,4-tetrafluoro-2,3,5,5-tetrachloro-Δ2-cyclopentene	15%
1,1,4-trifluoro-2,3,4,5,5-pentachloro-Δ2-cyclopentene	36%
1,4-difluoro-1,2,3,4,5,5-hexachloro-Δ2-cyclopentene	35%
Hexachlorocyclopentadiene	6%
others	8%

- 15 The fraction of the product which condensed in the solid carbon dioxide/acetone trap (25 g) was found to contain 25.2% by weight of fluorine and included perchloroethylene.

WHAT WE CLAIM IS:—

- 20 1. A process for the halofluorination of hydrocarbons selected from straight chain saturated hydrocarbons and straight chain ethylenically unsaturated hydrocarbons each having up to 15 carbon atoms in the molecule, which comprises the step of reacting the hydrocarbon in the vapour phase and at a temperature of from 200 to 650° C. simultaneously with hydrogen fluoride and chlorine, bromine or iodine in a reactor in the presence of elemental carbon and, at least when the process is the chlorofluorination of methane, in the absence of any metallic halide catalyst; the reaction being conducted at a pressure of at least 0.5 atmosphere and with a residence time of reactants in the reactor being from 0.1 to 200 seconds.
- 25 2. A process according to Claim 1 in which the reaction is conducted, and the reaction product is collected, at the same pressure of from 5 to 15 atmospheres.
- 30 3. A process according to Claim 1 in which the hydrocarbon is methane, the reaction temperature is from 200 to 500° C., the reaction pressure is from 0.5 to 2 atmospheres, and the residence time of the reactants in the reactor is from 10 to 100 seconds.
- 35 4. A process according to Claim 3 wherein the reaction temperature is from 400 to 500° C.
- 40 5. A process according to any preceding claim wherein the pressure is atmospheric pressure.
- 45 6. A process according to Claim 1 in which the hydrocarbon contains from 2 to 15 carbon atoms in the molecule, the reaction is conducted at a temperature of from 200 to 600° C. at atmospheric pressure and the residence time of the reactants in the reactor is from 1 to 100 seconds.
- 50 7. A process as claimed in Claim 6 wherein the hydrocarbon contains from 3 to 15 carbon atoms and is reacted with chlorine under such conditions of temperature, residence time and proportion of reactants that the product contains at least one chlorofluoromethane.
- 55 8. A process according to Claim 6 in which the temperature is from 400 to 500° C.
- 60 9. A process according to either Claim 6 or Claim 8 in which the reaction is conducted in the absence of a metallic halide catalyst.
- 65 10. A process according to any preceding claim in which the carbon is employed as a static bed.
- 70 11. A process according to any preceding claim in which there is maintained in the reactor a temperature gradient rising from below the reaction temperature to the reaction temperature and in which at least one of the reactants is introduced into the reactor at a temperature below the reaction temperature.
- 75 12. A process according to Claim 11 in which all the reactants are introduced into the reactor in admixture and at a temperature below the reaction temperature.
- 80 13. A process according to any preceding claim in which a diluent gas is introduced with the reactants into the reactor.
- 85 14. A process according to Claim 13 in which the diluent gas is nitrogen.
- 90 15. A process according to any preceding claim in which the halogen is chlorine.
- 95 16. A process according to any of Claims 1 to 14 wherein the halogen is bromine.
17. A process as claimed in Claim 1 for the production of cyclic chlorofluoro-compounds having a five-membered carbon ring wherein n-pentane is reacted in the vapour phase at a temperature of from 200 to 650° C. simultaneously with hydrogen fluoride and

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1,077,932

- chlorine in a reactor in the presence of elemental carbon, the reaction being conducted at a pressure of at least 0.5 atmospheres and with a residence time in the reactor of from 0.1 to 200 seconds.
18. A process as claimed in Claim 17 substantially as described with reference to Example 17.
19. A process for the halofluorination of hydrocarbons substantially as described in the Examples.
20. Halofluorecompounds whenever prepared according to the process of the present invention.

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